

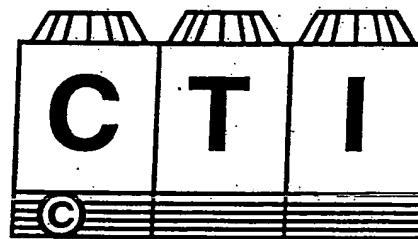
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COOLING TOWER INSTITUTE

ORGANIC HALOGEN STABILIZERS

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The studies and conclusions reported in this paper are the results of the author's own work. The paper has been presented before, and reviewed by the Cooling Tower Institute, and approved as a valuable contribution to cooling tower literature.

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INTRODUCTION

BCDMH, 1-bromo, 3-chloro, 5,5-dimethylhydantoin, is a relatively new disinfectant. It was developed in the late 1950s and first introduced to the cooling water systems in January 1980 under the trademark BromiCide [Sargent (1986)]. During the last several years, it has gained popularity for use in cooling water systems. However, the reports about the disinfecting efficacy of BCDMH are confusing and contradictory. Patterson [1957] and Hugo [1971] claimed that BCDMH was a better disinfectant against bacteria than chlorine. Macchairola *et al.* [1980 and 1981] found from field tests that BCDMH was 10 to 20 times as effective as chlorine in controlling biofouling in cooling water systems. Some people in the cooling water industry indicated that BCDMH was several hundred times more effective than chlorine and was a magic disinfectant against microorganisms. Fliermans and Harvey [1984], however, observed in field tests of industrial cooling towers, at the concentration recommended by the manufacturer, that neither the density nor the activity of *Legionella pneumophila* was affected by BCDMH. The same tests showed chlorine was effective against this microorganism. They also showed that even when the concentration of BCDMH was increased up to 10 times the level recommended by the manufacturer, BCDMH was ineffective against *L. pneumophila*. Soracco *et al.* [1985] compared the killing power of BCDMH to chlorine in antifouling treatment regimes. They concluded that, in general, BCDMH and chlorine displayed similar biocidal efficacy and there seemed to be no advantage to the use of BCDMH.

Fliermans and Harvey [1984] proposed that the difference in results between their field tests and the manufacturer's claim was probably due to the different test conditions; the manufacturer performed tests in the lab only, while they conducted their tests in the field. Sometimes the lab results fail to get responses similar to the field tests. Manufacturers, like the Great Lakes Chemical Corporation [Macchairola *et al.* (1980 and 1981)], however, claimed they conducted their tests both in the lab and in the field. Unfortunately, the results were not detailed. These contradictory points of view indicate that the effectiveness of BCDMH needs to be investigated further.

This research investigated the disinfection of BCDMH in detail. In experiments using various microorganisms, the disinfecting ability of BCDMH was compared to different inorganic and organic disinfectants under varied test conditions. The disinfecting mechanism of BCDMH was investigated through studying its hydrolysis products and

ORGANIC HALOGEN STABILIZERS

Mechanisms and Disinfection Efficiencies

ABSTRACT

Reports on the disinfection effectiveness in cooling water of some organic halogen stabilizers, such as 1-bromo, 3-chloro, 5,5-dimethylhydantoin (BCDMH), are quite contradictory and confusing. What is the truth about these compounds? This research investigated the disinfection efficiency and mechanism of BCDMH in detail, and compared the results with a variety of inorganic and organic disinfectants, in particular, a mixture of chlorine and bromide ions. Tests were conducted under different environmental conditions using several types of microorganisms. Various instruments and methods were used in investigating the mechanism of how BCDMH works as a biocide.

comparing the disinfection effectiveness of BCDMH with chlorine, bromine and their inorganic mixture, CCDMH, and its mixture with bromine compounds.

MATERIALS AND METHODS

1. Investigation of Disinfection Efficiency

The tests were conducted at a constant temperature ($21 \pm 2^{\circ}\text{C}$). The key variables used in the laboratory study of disinfecting efficiency were as follows: pH, ranging from 6.5 to 8.5; different ammonia nitrogen concentrations ranging from 0 to 15 mg/L; variable disinfectant concentrations ranging from 0.1 to 15 mg/L as chlorine; and different concentrations of DMH, salts and hardness.

Chemicals BCDMH, CCDMH and BBDMH were prepared in the Lab of Environmental Engineering Program, University of Houston, Houston, Texas; but part of the BCDMH compounds were commercial products. All these three chemicals, whether prepared in the lab of University of Houston or supplied by the related company were not reagent grade. DMH was in 98% purity. Reagents sodium hypochlorite, liquid bromine, sodium bromide, sodium sulfide, sodium chloride, ammonia chloride, sodium hydroxide and the other chemicals used for the tests were ACS certified unless otherwise mentioned. The validity of using the DPD-FAS and Amperometric Methods to measure the halogen contents in BCDMH, CCDMH, and BBDMH was justified prior to this test [Zhang, 1988].

The microorganisms studied in this research included three pure bacteria cultures (*E. coli* ATCC 25922 and *E. aerogenes* ATCC 13048 and *P. aeruginosa* ATCC 27853) and one mixed culture (Polybacteria). The Polybacteria used in this research is a product by Polybac Corporation named Hydrobac. The culture suspension was prepared according to AOAC [1984]. The disinfection tests and the preparation of the reagent solutions were conducted according to the methods described in the Official Methods of AOAC [AOAC (1984)], Standard Methods [APHA (1985)] and Aquatic Microbiology Laboratory Manual [Cooper *et al.* (1976)].

2. Study of the Hydrolysis Products and Mechanisms

The chemicals BCDMH, CCDMH and BBDMH used in this part were the same as those specified before. The other chemicals used were described in the related methods [Zhang, 1988]. The titration was conducted by the DPD-FAS, Amperometric, and the other methods. A Model 397, Fisher Cl₂ Titrimeter was used for the Amperometric Method. A Model TOX-10, MCI (Mitsubishi Chemical Industries Limited) Total Organic Halogen Analyzer was used for the TOX test.

The Mass Spectrometer, Model HP5988, was used for the MS analysis of the HPLC/MS test. BCDMH solution was prepared with HPLC pure water and all of the attached mass spectra were obtained by pumping freshly prepared solutions of DMH, BCDMH, CCDMH and BBDMH directly into the mass spectrometer via a Vestec Thermospray LC/MS interface. The mass spectra generated were a result of scanning the mass spectrometer in the negative ion mode from 30 to 300 AMU (Atomic Molecular Units).

The IC analyses were conducted on a Dionex, Model 16, Ion Chromatograph. The IC instrument was equipped with a Hewlet Packard Reporting Integrator, Model 3390 A, and a Fisher Recordall Recorder, Series 5000. All the solutions were prepared with Chlorine Demand Free (CDF) water or their equivalent NanoPure water.

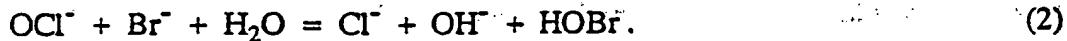
RESULTS AND DISCUSSION

The results are summarized in Figures 1 to 5. The results demonstrated the followings:

1. Disinfection Efficiency

(1) At low pH values, e.g., pH 6.5, BCDMH had disinfecting efficiency slightly lower than chlorine. However, at higher pH (pH 8.5), BCDMH was more efficient than chlorine against all the four types of test microorganisms. This advantage was mainly attributed to the higher pK value of HOBr. HOCl and HOBr are neutral species, and they are much more effective in killing microorganisms than their analogous OCl⁻ and OBr⁻, which are negatively charged and poor disinfectants.

In the BCDMH solution, another reaction was also going on, at least partially. That was the oxidation of bromide to HOBr (OBr^-) by OCl^- (HOCl), which was also responsible for the higher killing efficiency of BCDMH at high pH than chlorine alone since it increased the total amount of HOBr,



These reactions occur very rapidly in the entire pH range from 4 to 10. At pH 7 to 9, reactions go quantitatively and almost instantaneously [Farkas *et al.* (1949)]. This reaction adds an additional advantage to the disinfecting effectiveness of BCDMH.

(2) The inorganic mixture of bromine and chlorine at 1:1 molar ratio exhibited disinfecting efficiency against the tested microorganisms similar to BCDMH at pH 6.5. And the solution of DMH did not have any killing efficiency at all. These facts indicated that DMH did not display any disinfecting function; it just worked as a reservoir to store halogens. The results also suggest that BCDMH was not a magic disinfectant.

(3) In the presence of ammonia and at pH 7.0, BCDMH was a superior disinfectant compared to chlorine. Bromine had better disinfecting power than BCDMH in the presence of ammonia. This fact indicated that the superior disinfecting ability of BCDMH to chlorine in the ammonia containing solution might be attributed to the superior disinfecting efficiency of bromamines compared to chloramines.

(4) The addition of the bromide ions to the chlorination system enhanced the disinfecting effectiveness of chlorine both at high pH values and in the presence of ammonia nitrogen. The mixture of chlorine and sodium bromide with equal molar ratio was as effective as bromine both at higher pH values and in the presence of ammonia. In this mixture solution, Br^- was oxidized to HOBr. So the mixture of chlorine and bromide ions can be used to substitute for the bromine solution. The former, of course, is much easier to prepare. Given the $\text{NH}_3\text{-N}$ and chlorine concentrations were 2.0 mg/L, respectively, the addition of 10% and 20% (molar ratio) of sodium bromide to the NaOCl solution (and then the addition of the chlorine-bromide solution to the sample containing ammonium ions at pH 7.0) increased the disinfecting effectiveness against *E. coli* from 9.1% to 92% and 99% separately at 1 minute contact time. Against Polybacteria, given the $\text{NH}_3\text{-N}$ and chlorine concentrations were 6.0 mg/L separately, the addition of 10% and

20% (molar ratio) of sodium bromide raised the percentage kill from 6% to 68% and 81%, respectively.

The procedure of how to add and when to add bromide ions was critical to the improvement on the chlorine disinfection. Three different methods were compared to each other. They were:

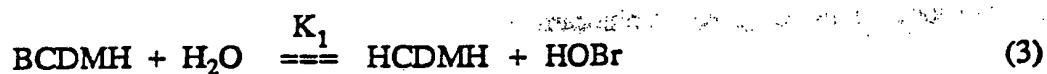
Method A: Mix chlorine and ammonia first, then add bromide to the mixture;

Method B: Mix bromide and ammonia first, then add chlorine to the mixture;

Method C: Mix chlorine and bromide first, then add the mixture to the ammonia solution.

Method C exhibited the best improvement of bromide ions on disinfection of chlorine among the three methods tried. No significant improvement was observed from Method A. When Method B was applied, the results of disinfecting efficiency of the test solution were between the above two cases, but the improvements were not as stable, depending on the operating conditions.

(5) The experimental results indicate that the increase in the concentration of DMH negatively affected the disinfecting efficiency of BCDMH. The high concentration of DMH changes the equilibrium between DMH, the released halogens and HCDMH. With the increase of the concentration of DMH, the available concentrations of halogens at equilibrium decreases.



$$K_1 = \frac{[\text{HOBr}][\text{HCDMH}]}{[\text{BCDMH}]} \quad (5)$$

$$K_2 = \frac{[\text{DMH}][\text{HOCl}]}{[\text{HCDMH}]} \quad (6)$$

$$[\text{HCDMH}] = \frac{[\text{DMH}][\text{HOCl}]}{K_2} \quad (7)$$

$$[\text{HOBr}] = \frac{K_1[\text{BCDMH}]}{[\text{HCDMH}]} \quad (8)$$

$$= \frac{K_1 K_2 [BCDMH]}{[DMH][HOCl]} \quad (8)$$

$$[HOBr][HOCl] = \frac{K_1 K_2 [BCDMH]}{[DMH]} \quad (9)$$

K_1 and K_2 are constants. At a given concentration of BCDMH, the concentration product of HOBr and HOCl is inversely proportional to the concentration of DMH. The higher the concentration of DMH, the lower the concentrations of HOBr and HOCl. The decrease of the total available concentration of halogen leads to the lower killing efficiency. During the disinfecting process of a cooling tower, BCDMH may result in accumulated DMH.

(6) Among the four types of microorganisms tested, Polybacteria was the most resistant against both BCDMH and chlorine, while *E. coli* was the least resistant against the applied disinfectants under the tested conditions. The sensitivities of *P. aeruginosa* and *E. aerogenes* against the tested disinfectants were between *E. coli* and Polybacteria.

(7) To evaluate or compare disinfecting effectiveness, various criteria are available. For example, disinfectants can be compared to each other on their required minimum residual concentration or dosage, or on contact time to meet a given killing percentage for the same dosage. Disinfectants can also be compared on the basis of a short contact time or a relatively long contact time. In this research, short contact time or quick kill test was used for the comparison of BCDMH against the other disinfectants. However, in water treatment systems like cooling towers, both the disinfecting effectiveness of a short contact time and the total contact time should be taken into consideration in order to have a better evaluation. According to Morris [Johnson (1975)],

$$N_t = N_0 \exp \left(- \sum_{i=1}^t \lambda_i \Delta t_i \right) \quad (10)$$

where

λ_i = the susceptibility coefficient, a reflection of ease or rapidity with which the microorganisms are destroyed or inactivated

$$\lambda_i = L C_i$$

C_i = concentration of a disinfectant "i", mg/L

L = the specific susceptibility coefficient

N_0 = the microorganism concentration at $t = 0$, CFU/mL

N_t = the microorganism concentration at time t , CFU/mL

t = contact time, minutes.

When l_i is a constant, the data of N_t conform to Chick's Law.

2. The Hydrolysis Process of BCDMH and Mechanisms

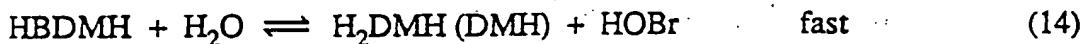
(1) The results of different titration methods and the results from the Total Organic Halogen (TOX) and Ion Chromatography (IC) tests indicated that both the Amperometric and DPD-FAS Methods could be used to determine the halogen concentrations of BCDMH, CCDMH and BBDMH within the experimental error. The results also demonstrated that BCDMH could release all of its halogen contents under the titration conditions investigated. The TOX test results indicated that no organic halides were contained in BCDMH, CCDMH and BBDMH.

(2) For the same sample, the results obtained from IC analysis and the results obtained from the Amperometric and the DPD-FAS Methods were in close agreement. This fact indicated that under the reducing conditions of phenylarsine oxide solution, ferrous ammonium sulfate, sodium sulfide and sodium thiosulfate, all the chlorine and bromine contained in BCDMH, CCDMH and BBDMH were reduced completely to chloride and bromide ions. At the same time, the test also showed the Amperometric and the DPD Ferrous Titrimetric Methods could be used satisfactorily to analyze the total available chlorine and bromine concentrations in BCDMH, CCDMH and BBDMH.

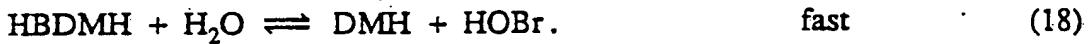
(3) The results of HPLC/MS showed that HCDMH was in much higher abundance than BCDMH. Therefore, bromine in the BCDMH was more readily hydrolyzed than chlorine.

(4) The hydrolysis pathway of BCDMH can be expressed as





A basic pH condition can accelerate the hydrolysis of BCDMH. Similar hydrolysis pathways can be written for the hydrolysis processes of CCDMH and BBDMH.



CONCLUSIONS

1. The results of the comparison showed that at low pH values, e.g., pH 6.5, BCDMH had disinfecting efficiency slightly lower than chlorine against the tested microorganisms in the chlorine demand free water. BCDMH was 3 to 4 times as effective as chlorine at pH 8.5; and in the presence of ammonia nitrogen at pH 7.0, BCDMH was about 20 times or more as effective as chlorine alone. In contrast, BCDMH was less effective in disinfection than bromine both at pH 8.5 and in the presence of ammonia nitrogen at pH 7.0. The accumulation of DMH greatly decreased the effectiveness of BCDMH, particularly, at high [DMH]/[BCDMH] molar ratios.

2. The addition of bromide ions to the chlorine solution greatly improved the chlorine disinfecting ability at higher pH values (pH 8.5) and in the presence of ammonia nitrogen. A mixture of bromide and chlorine at 1:1 molar ratio showed disinfecting effectiveness similar to bromine, and was superior to BCDMH under the above test conditions. In the presence of ammonia nitrogen, the technique for adding bromide ions was, however, critical to the improvement of the disinfecting efficiency of chlorine. Three different ways were tried to add bromide ions to the chlorination system containing ammonia nitrogen. Among them, the method showing the best result for improving the disinfecting efficiency was to mix the bromide ions with chlorine first and then use the mixture to disinfect the sample solution containing ammonia nitrogen. The preparation of

the mixture of bromide ions with chlorine is easier than synthesizing BCDMH. Also, the cost of this mixture is less expensive.

Therefore, making a product that can provide a separate chlorine and bromide source to minimize the loss because of bromine in BCDMH would be attractive. This new product can also overcome the shortcomings of poor solubility of BCDMH. The new product should consist of two parts. One is an organic containing chlorine that acts as a chlorine reservoir, slowly releasing chlorine; the other part of this product is sodium bromide, which provides bromide ions.

3. The results revealed that the disinfecting power of BCDMH was mainly attributed to its hydrolysis products HOBr/OBr^- and HOCl/OCl^- . During the hydrolysis process, BCDMH released bromine faster than chlorine.

4. The hydrolysis pathway of BCDMH can be expressed as shown in the Equations 11 through 14.

ACKNOWLEDGMENT

The authors are very grateful for the financial support of the Applied Biochemists Inc. and Monsanto Chemical Company, which made this research possible.

A = NaOCl, 0.1 mg/L B = NaOCl
 C = Bromine D = NaOCl, 0.1 mg/L
 E = BCDMI F = BCDMI
 G = BBDMI H = BBDMI + Br-
 I = NaOCl + Br- J = BBDMI + Cl-
 K = NaOCl + HOBr

(All the concentrations of disinfectants are 0.2 mg/L
as chlorine unless otherwise specified)

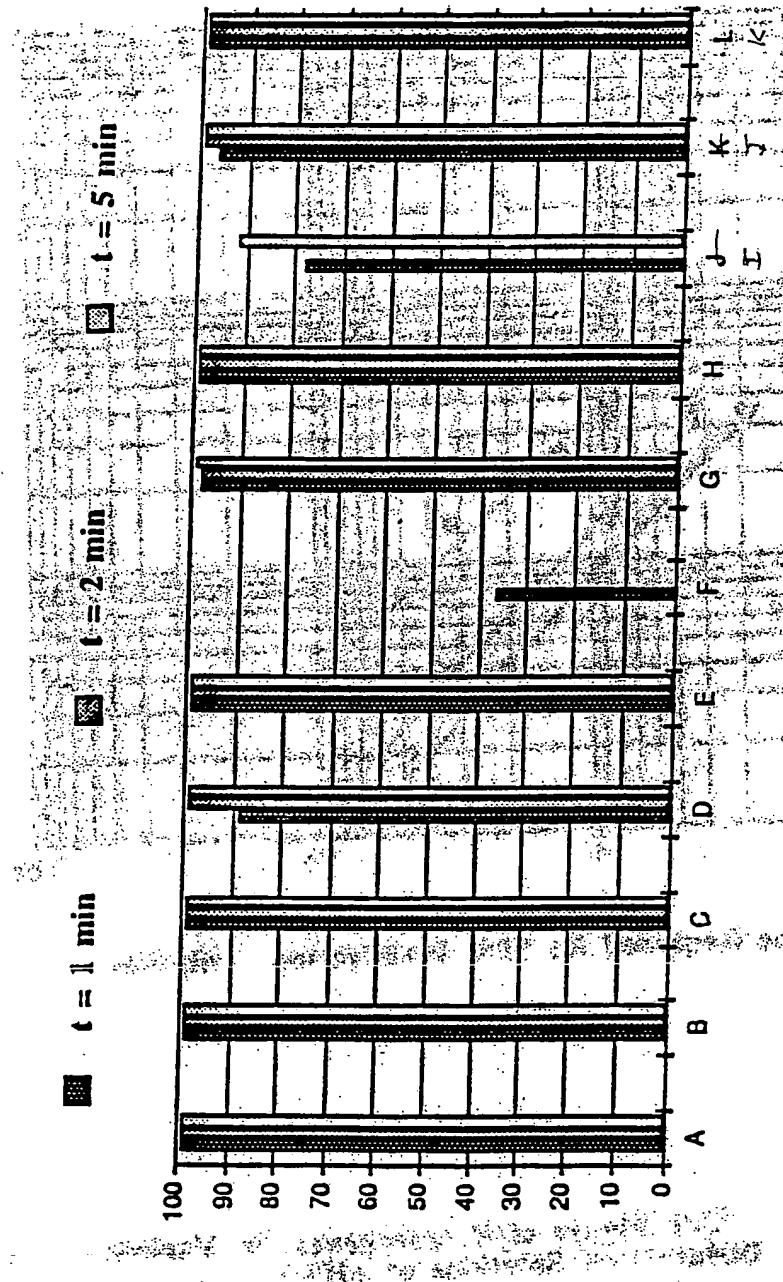


Figure 1. Comparison on Disinfecting Efficiency of Different Disinfectants Against *E. coli* at pH 6.5

- FACl (Free Available Chlorine)
- FABr (Free Available Bromine)
- BCDMH

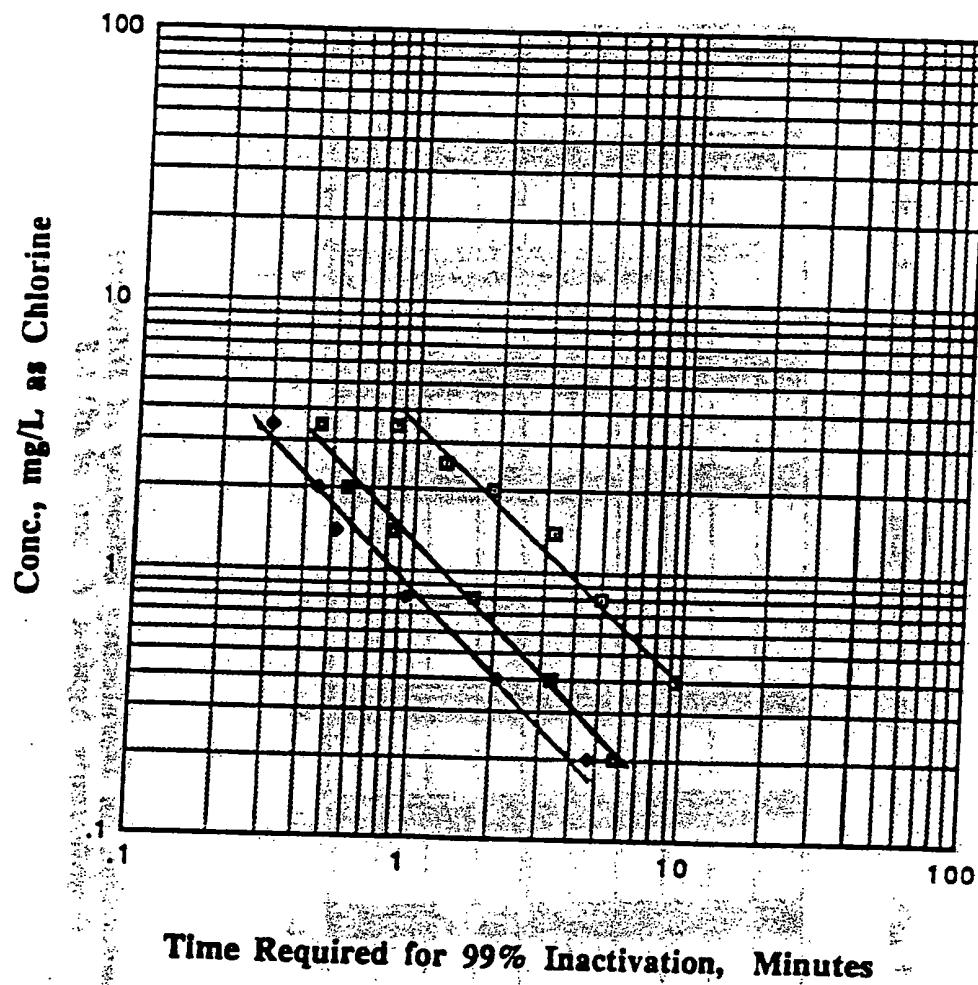


Figure 2. C-T Figure of *E. aerogenes* in Various Disinfectant Solutions at pH8.5

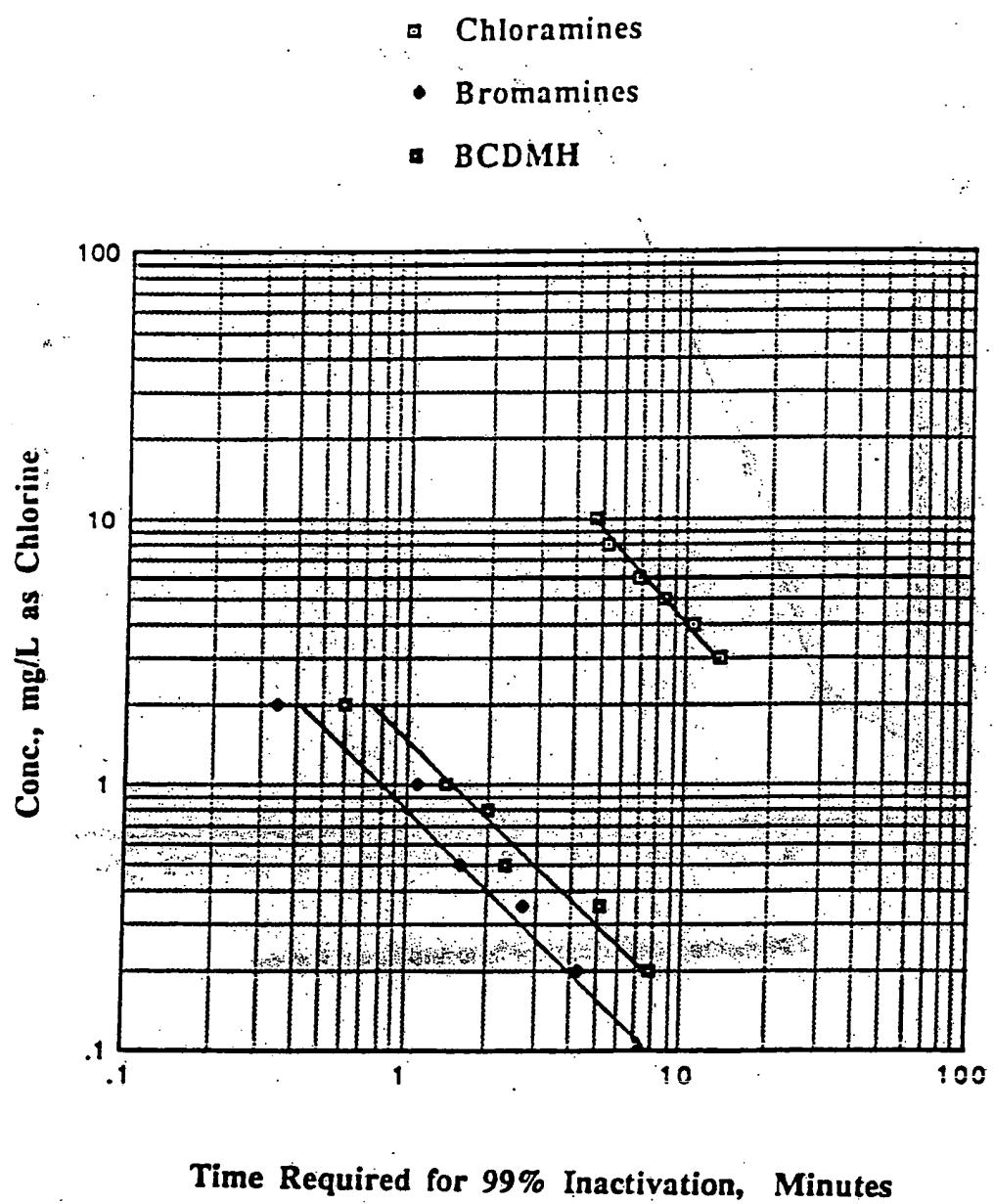


Figure 3. C-T Figure of *P. aeruginosa* in Various Disinfectant Solutions Containing NH₃ ([Cl₂]/[NH₃·N] Weight Ratio = 1, pH = 7.0)

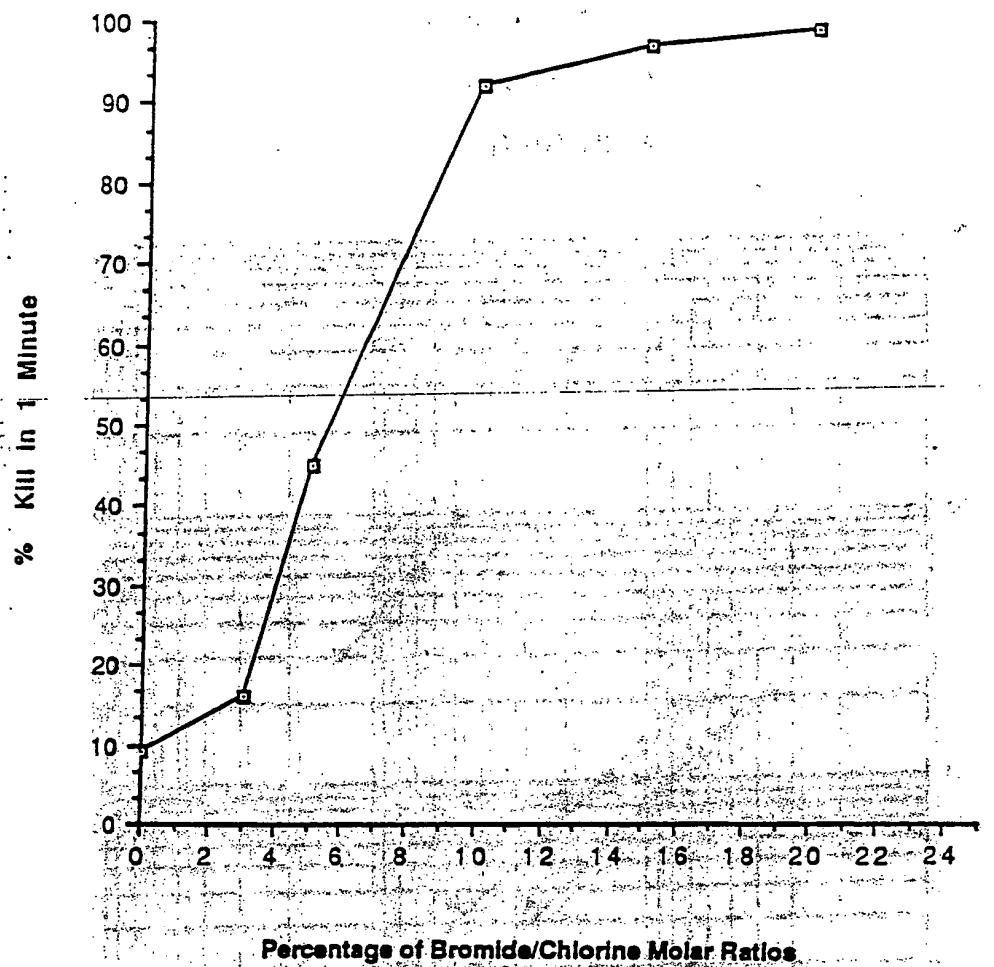


Figure 4. Bromide/chlorine Ratios and Killing Efficiency Against *E. coli* in the Solution Containing Ammonia ($[Cl_2]$ and $[NH_3]$ = 2.0 mg/L, respectively)

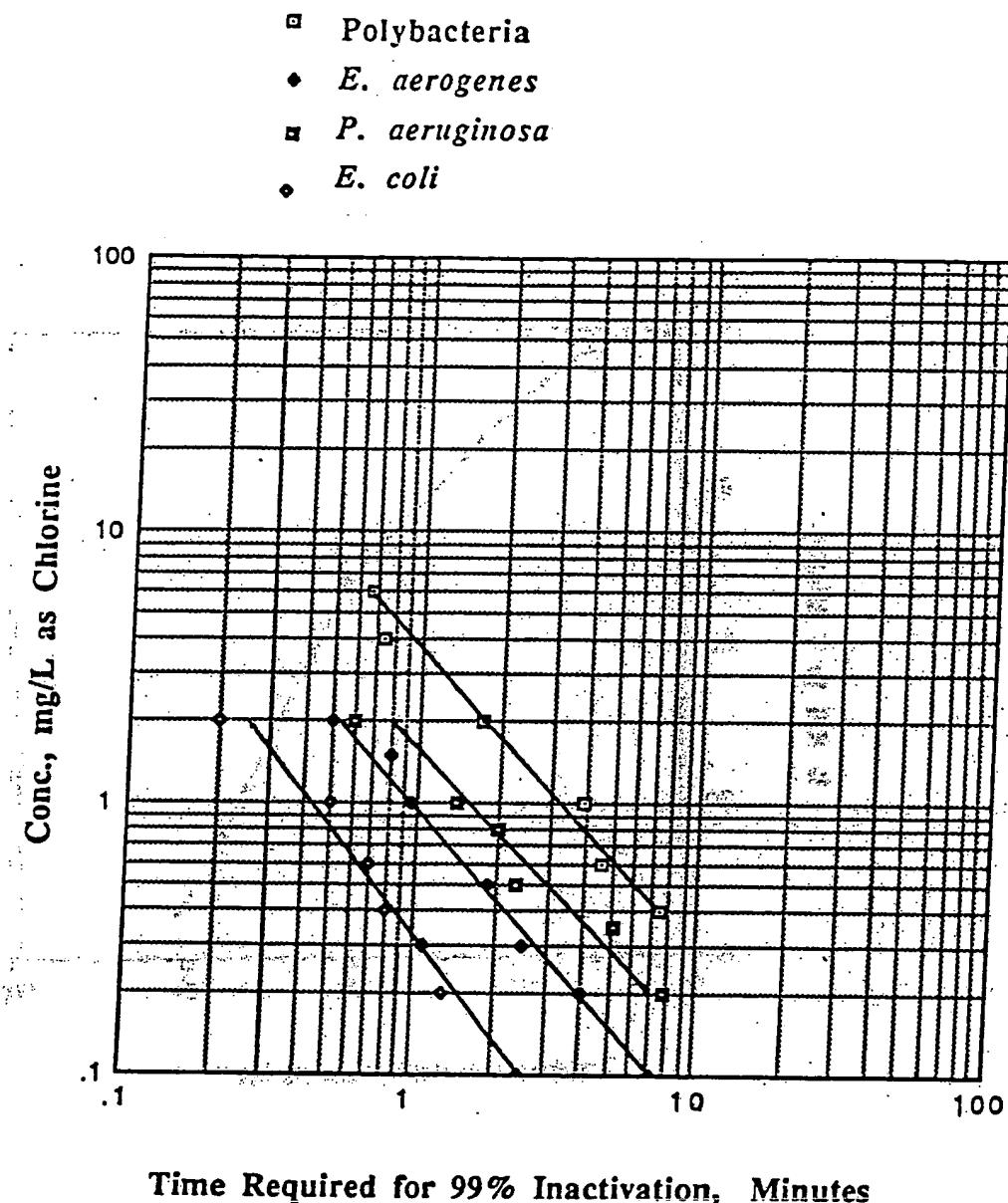


Figure 5. C-T Figure of BCDMH Against Different Microorganisms Containing NH₃ ([Cl₂]/[NH₃-N] Weight Ratio = 1)

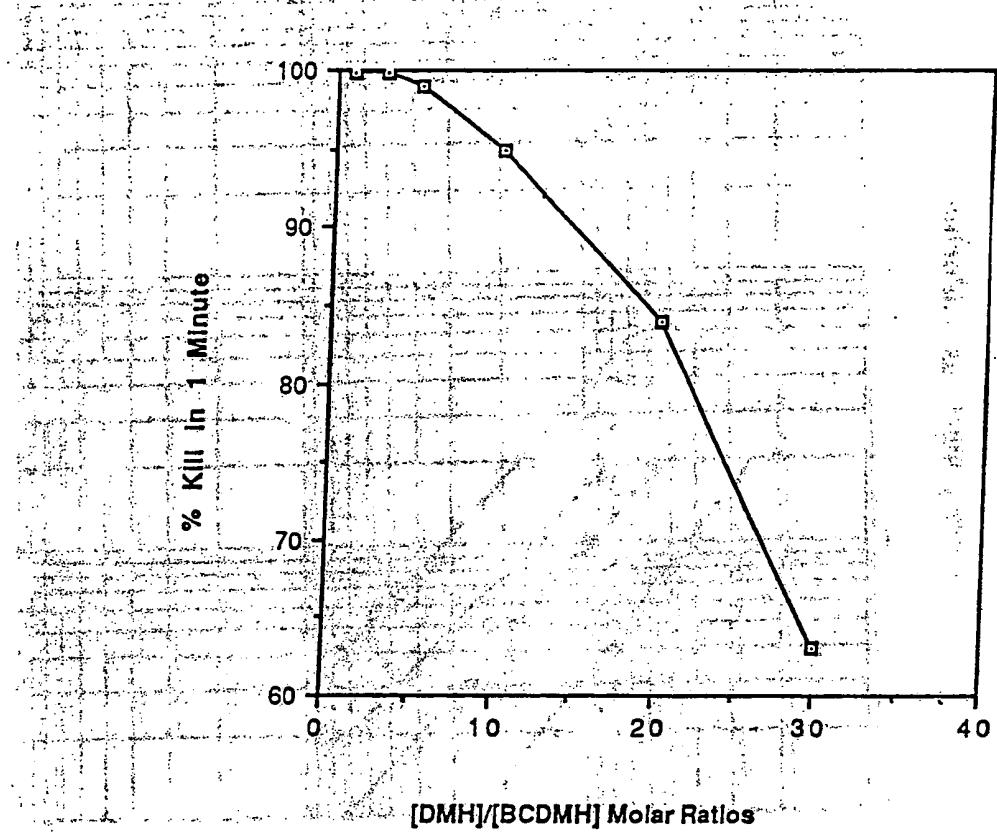


Figure 6. Effect of DMH Concentrations on the Disinfecting Efficiency of BCDMH
($[BCDMH] = 0.2$ mg/L as Chlorine)

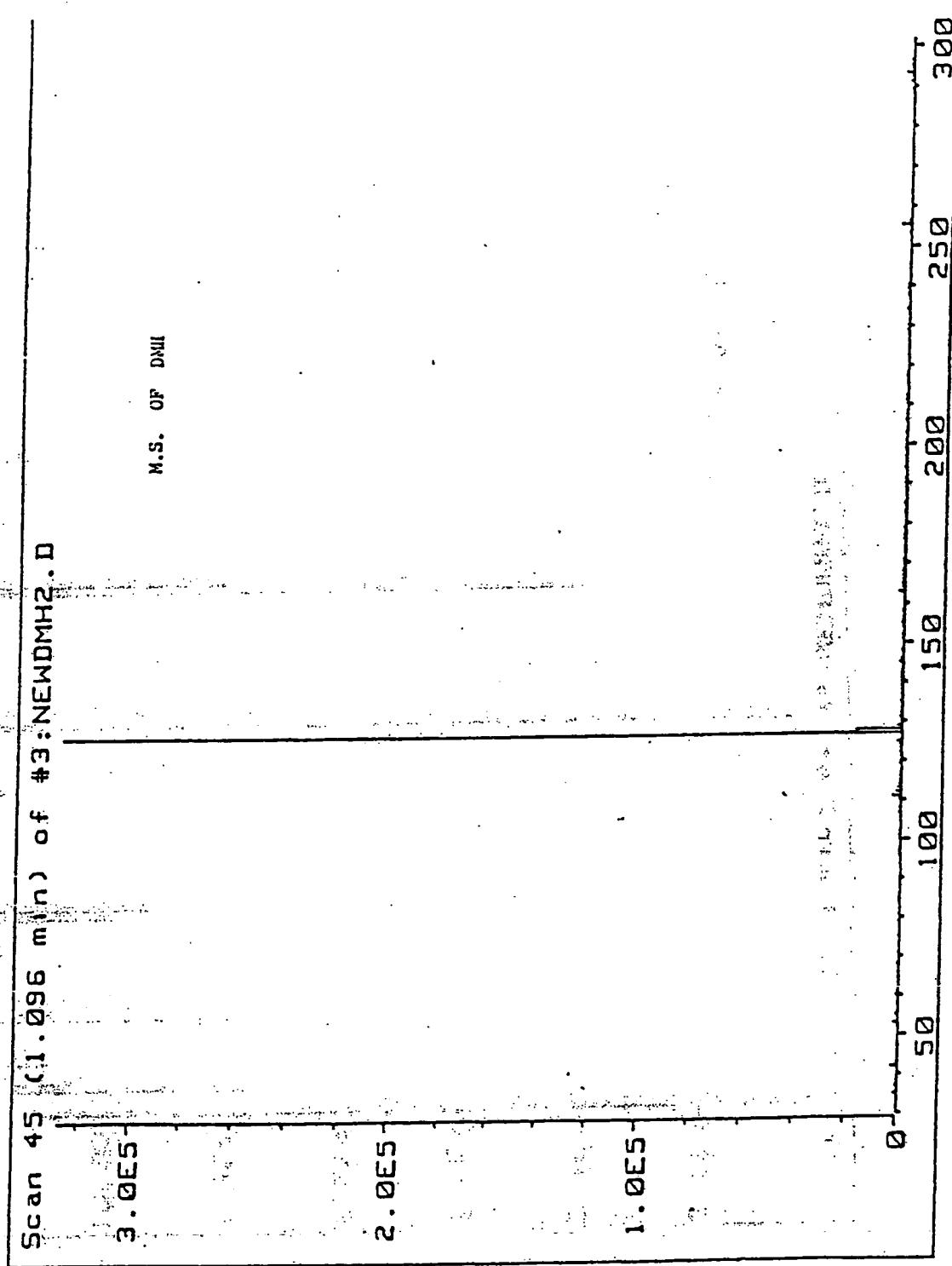


Figure 7. MS Spectrum of DMU from the HPLC/MS Test

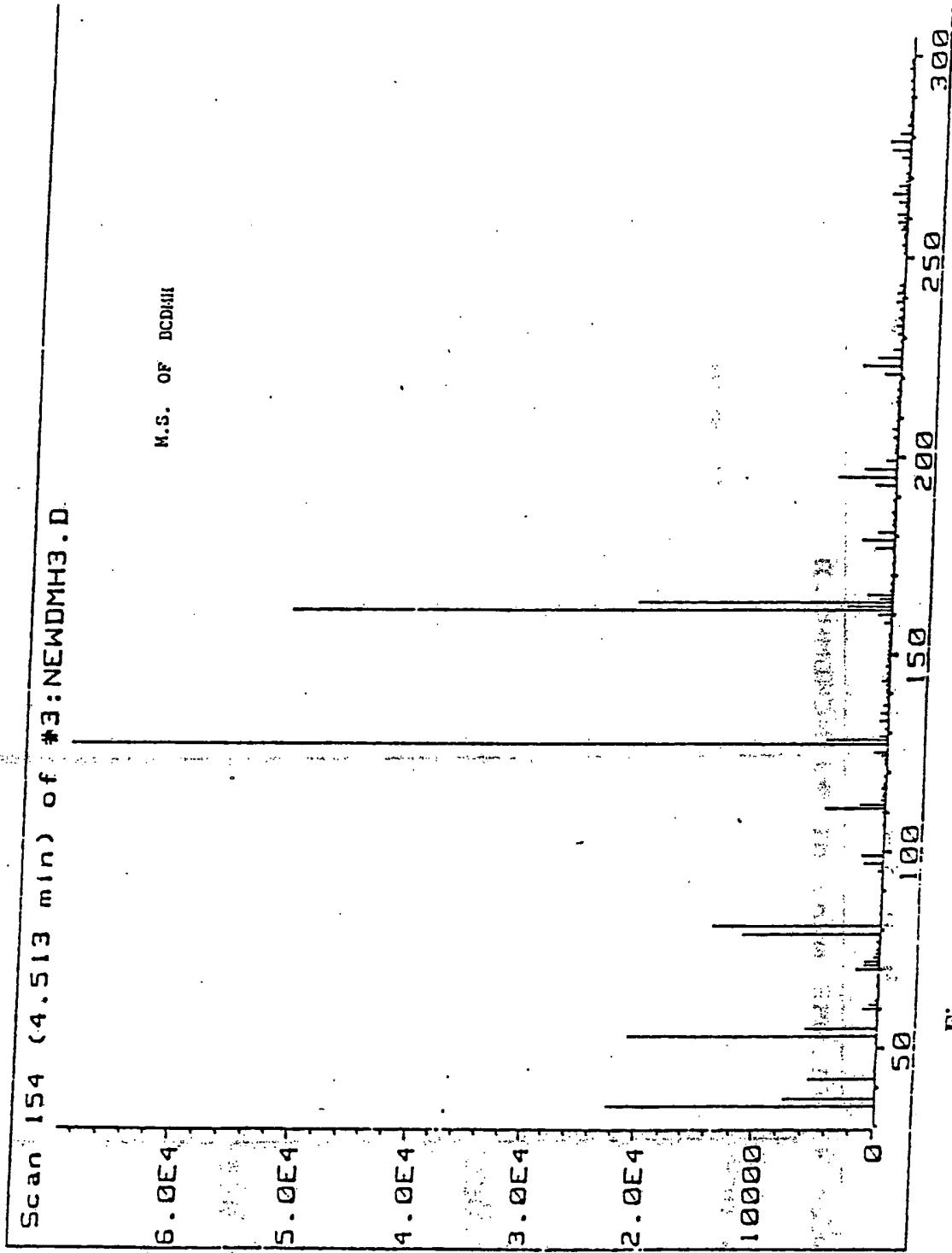


Figure 8. MS Spectrum of BCDMH from the HPLC/MS Test

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